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TITANIUM OXIDE NANOCOMPOSITE MATERIALS: SYNTHESIS, CHARACTERIZATION AND ITS SOLAR APPLICATION

Cahyorini Kusumawardani

Department of Chemistry Education, Yogyakarta State University, Yogyakarta, Indonesia, 55281
Email: cahyorini.k@uny.ac.id, irienuny@yahoo.com

Abstract

Titanium oxide (TiO_2) is one of the powerful semiconductors in solar application and now attracted high attention on photovoltaic technology because it has highly stability, activity, high surface area and easily to prepare. Since TiO_2 only active in ultraviolet region, it needs the use of other materials on TiO_2 to provide a higher efficiency for practical application. Nanostructure material offers an ease tailoring of optical properties from its spatial quantum confinement. The quantum size semiconductors can be applied on TiO_2 to result nanocomposites with a high degree of flexibility to alter and control their properties and functionalities. Titania nanocomposites synthesis are developed to produce a superior materials for solar harvest and conversion with the focus on tuning bandgap energy, overcoming the limit of transport electrons and holes, reducing the electron-hole recombination and also reducing production cost. The titanium oxide nanocomposites have great potency for solar application as semiconductors on solar cells device, powerful photocatalyst for water and air purification, water splitting system and hydrogen generation system.

Key words: nanocomposite, nanostructure, quantum size, titanium oxide, solar application

Introduction

The oil crisis that occurred in 1973 has encouraged a rapid development and research in the field of photoelectrochemical as a potential energy source alternative (Kalyanasundaram, 1985). Since the first water photolysis reported by Fujishima and Honda (1972), TiO_2 became the most favored semiconductor material in photoapplication technologies. TiO_2 is a powerful semiconductor since it has widely band gap energy, quite inert, highly thermal and chemical stability, high activity, high surface area, easily to prepare and is one of the most available elements in the world. However, the intrinsic wide band-gap nature (around 3.2 eV) makes TiO_2 is only active in UV region, which is only a very small part of sunlight (Qiu and Burda, 2007). The improvement of TiO_2 photoactivity is designed to red-shift the absorption edge which is less energetic but more intense visible part of the solar spectrum (Horikawa *et al.*, 2008).

The development of dye-sensitized solar cells (DSSC) by Oregan & Gratzel in 1991 leaded TiO_2 as a powerful semiconductor in solar application. DSSC provide a concept in separation of optical absorption and charge generating functions for efficient absorption of sunlight by using an electron transfer sensitizer. In the DSSC system, the enhancement of TiO_2 response was achieved by anchoring organic dyes as sensitizers, which are usually Ru(II) complexes, to harvest the visible light. The DSSC system obtained an overall power conversion

efficiency of 12% for small cells and about 9% minimodules (Hagfeldt *et al.*, 2010). The dye-sensitized TiO_2 was successfully enhancing the solar spectrum absorption to the visible light, but this solar system is still facing several problems for commercial application due to the degradation of dye sensitizer and liquid electrolyte that lower the solar system efficiency and stability. Therefore, it needs to modify the DSSC system in order to overcome the limitation of currently system.

The use of tandem semiconductors in the solar system is being an alternative to solve the problems appeared from the dye photodegradation. The first report on the use of quantum dots (QDs) instead of dye to sensitize semiconductor oxide matrix as light absorber on quantum dots sensitized solar cells (QDSSC) was done by Serpone *et al.*, 1984. QDSSC has a higher absorption, greater stability, wider tunable responsible wavelength range than the DSSC system, and also importantly the possibility to exploit multiple exciton generation and utilize hot electrons whose energy is higher than the low limit of TiO_2 conduction band (Nozik, 2002). The solar efficiency of liquid junction QDSSCs has reach 4.9% at present (Hodes, 2008) but it highly potential to increase the efficiency of this solar system by tuning several properties of the quantum dots (Zhang *et al.*, 2011). The name of the third generation solar cells are given to this devices (Green, 2003). In principle, sunlight can be converted to electricity at efficiency close to Carnot limit of 93%. QDSSCs are very promising third generation solar cells due to their potential of achieving competitive cost-efficiency ratio.

The future solar device will be based on nanocomposites materials including tandem nanostructured semiconductors, organic-inorganic hybrid assemblies and nanomolecular assemblies to obtain high efficiency at an economically viable cost (Kamat, 2007). Nanostructures provides spatial quantum confinement for tuning the optical properties of semiconductor nanomaterials, so the use of nano-multicomponents offers a flexibility to alter, control and functionalize the properties of nanocomposites. Nanocomposite materials are designed to optimize the solar device performance because it overcome the limits of single materials in solar spectrum response (band gap engineering), transport of electrons or holes (defect engineering), reaction of electrons or holes with chemicals (catalyst engineering), and reduce of costs (economic consideration). This article reported the study on the synthesis, characterization of titanium oxide/quantum dots nanocomposites and its solar application.

TiO_2/Quantum Dots Nanocomposite

Semiconductor quantum dots (QDs) are strongly luminescent and exhibit significant optical and electronic properties that can easily be tuned according to their size by varying the preparation method and synthesis parameters (Bawendi *at al.*, 1990). Several QDs have been used as light harvesters in photovoltaic devices include CdS, CdSe, CdTe, $CuInS_2$, Cu_2S, PbS, PbSe, InP, Ag_2S and organo lead halide perovskite (Radich *et al.*, 2011; Tubtimtae *et al.*, 2010; Arup *et al.*, 2011; Gunes *et al.*, 2011). Their performances in the solar cell systems presented the research area to explore new semiconductors as light absorber in CD-based solar cells, which is called quantum dot-sensitized solar cells (QDSSD). The concept of QDSSC is following the DSSC, where the use of dye to sensitize TiO_2 is substituted by quantum dot materials. Due to the similar size of QDs and the nanocrystals of TiO_2, all quantum dot-sensitized TiO_2 are nanocomposites in tend to optimize the response to solar spectrum.

TiO_2/quantum dots nanocomposites have sufficiently high response in the visible light thus it highly potential to use in the solar cells system. Nanocomposites TiO_2/CdS, CdSe, and CdTe (Mora-sero and Bisquert, 2010) are currently reported as the best materials for QDSSC system. The efficiency and the stability of the solar system are highly dependent on the quantum dots size and shape. The use of quantum dots to substitute dye sensitizers offers several advantages:

(1) the band gap energy of quantum dots are tunable and in wider range, so it can be simply tuned by adjusting the size and the shape of QDs, and well match to solar spectrum (Gorer and Hodes, 1994);
(2) quantum dots have large absorption spectrum, the high extinction property of bulk semiconductors are also still preserved at the nanoscale (Hodes, 2008; Moreel *et al.*, 2007; Yu *et al.*, 2003);
(3) quantum dots can create multiple electron-hole pair per photon by using hot electrons (Klimov, 2006, Nozik, 2002); and
(4) quantum dots are superior resistance towards photobleaching over dye sensitizer, low cost, and easy to prepare (Hodes, 2008).

However, the best reported efficiencies of QDSSCs are still lower than DSSCs because the QDs formed multilayer adsorption while applied on TiO_2 surface so it might hindrance the electron transfer rate from QDs to TiO_2 as shown in Figure 1. Also, the presence of considerable surface charge traps on adsorbed QDs will possibly increases electron-hole recombination before the electron reached the conduction band of TiO_2. It remain the challenge to obtain the overall power conversion efficiency up to above 31% to commercialize the QDSSCs system as a renewable energy supplier. Thus, there are several efforts that can be done for enhancing the efficiency and the stability of the QDSSCs.

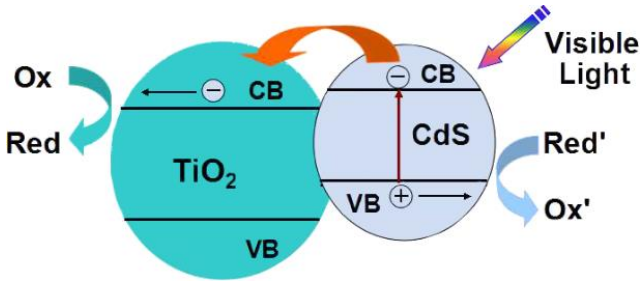

Figure 1 Scheme of TiO_2/quantum dots band gap energy position (Ruhle, 2010)

Figure 1 also showed the visible response of TiO_2/QDs nanocomposite, where the band gap energy of the used QDs are in the visible area. This will make the nanocomposite effectively absorb the sun light and continued by the electron injection from QDs to the conduction band of TiO_2. Quantum dots semiconductors has a higher band gap energy than bulk materials, due to the self-confinement effect (SCE). When the size of a material is decreased to a nanoscale size, the size of resulting exciton will become comparable or even greater than the particle. It will lead the bands energy splitting into discrete quantization levels and resulted a wider band gap. The experimental evidence of SCE is the excitonic peak to the higher energy in the optical absorption spectrum (blue shift) when the particle is decreased, so the difference between excitonic absorption and excitation into the conduction band (delocalized) becomes meaningless, as the exciton and the unoccupied states both are localized in this limit.

Synthesis of TiO_2/quantum dots Nanocomposite

The TiO_2/quantum dots nanocomposites can be synthesized characterized in two ways, namely ex situ (indirect) and in situ (direct) method. The ex situ method are synthesizing the TiO_2 and the quantum dots separately, then continued by coating the quantum dots on TiO_2 surface. Martinez *et al.* (2010) have synthesized CdS quantum dots through sol gel method using some polimers as stabilizing agents. The different stabilizing agents and different Cd:S molar ratio

resulted the different particle size, where the higher S composition leaded to the bigger particle size. As consequence, the bigger particle size provided smaller band gap energy. Al-douri *et.al.* (2013) had been synthesized CdS through sol gel method using thiourea as sulfide source before applying to TiO_2 for resulting TiO_2.CdS nanocomposite. It reported that the precursor's composition ratio had significant influence to the CdS structure and optical properties, thus affected the optical properties and photoactivity the nanocomposite. Quantum dots can also be synthesized using magnetron sputtering before applied to prepare nanocomposite as reported by Mora-sero & Bisquert. (2010) that synthesized TiO_2/CdSe and TiO_2/CdTe nanocomposites. Hensel *et al*. (2010) have synthesizes CdSe quantum dots using hydrothermal methods, where the synergistic effect of CdSe and nitrogen doping on TiO_2 provided the efficient effect on solar hydrogen generation. The ex situ synthesis of TiO_2/quantum dots nanocomposite are usually done by immersing the TiO_2 thin film in quantum dots suspension. The amount of optimum quantum dots content on TiO_2 is highly dependent on their both structural properties. The similar nanoscale size lead to the simpler and easier way to form nanocomposite. It is an easy way to control the structural and optical properties of both semiconductors by varying some synthesis parameters.

The other way to prepare TiO_2/quantum dots nanocomposites is through in situ method or direct formation of quantum dots on TiO_2 surface which is usually as a thin film. There are two common way to synthesize directly the TiO_2/quantum dots nanocomposites: SILAR (Successive Ionic Layer Adsorption and Reaction) and CBD (Chemical Bath Deposition). The SILAR method is used to create coatings on thin films for technological products such as solar cells. By allowing thin films to be coated in different chemicals at or close to room temperature, the TiO_2 thin films incorporating with quantum dots and avoid possible problems with damage caused by oxidation or corrosion. The SILAR method uses the transfer of ions that provides better coverage of chemicals over the fil, and can result in a finer grain structure than other deposition method. The main advantages of the SILAR deposition method include the ease of completing the method and relative low cost. The scheme of SILAR method showed in Figure 2.

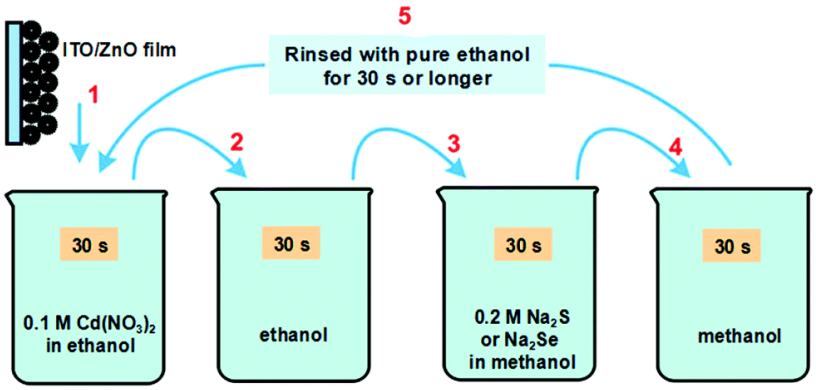

Figure 2 SILAR method for obtaining ZnO/Cds or ZnO/CdSe nanocomposites (ZnO can be replaced by TiO_2) (Yuan and Yin, 2014)

CBD (Chemical Bath Deposition) is also a kind of direct technique to obtain TiO_2/quantum dots nanocomposite. The main different between SILAR and CBD is that all compounds are mixed together before the immersion of TiO_2 thin film in the quantum dots solution. CBD is a convenient and low cost technique for producing large area thin fil semiconducting. Since this is a low temperature process, this avoids oxidation and corrosion of the substrate. These are slow processes, which facilitate better orientation of crystallites with improved grain structure. The number of possible materials to be produced through this technique is bound to multiply in subsequent years. The influence of growth parameters such as bath temperature, deposition rate, bath composition on various film properties need to be optimized to

obtained a functionalized nanocomposite. This method also need to use complexing agent like TEA (triethanolamine) to produce QDs on TiO_2 thin film. The equipment to proceed the CBD method for synthesizing nanocomposite showed in Figure 3.

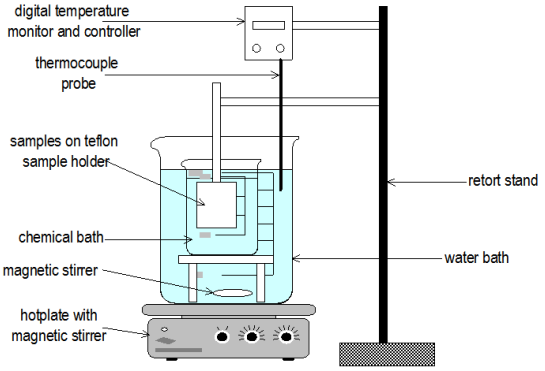

Figure 3 Equipment for chemical bath deposition technique (Musembi *et al*., 2013)

Characterization of TiO_2/QDs Nanocomposite

The TiO_2/quantum dots nanocomposite are characterized in order to determine the chemical composition, the morphology and of the produced structures are the expected ones. The structure of nanocomposite is characterized by X ray diffraction (XRD) in the range 20-90 ºC. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) are used to study the morphology of the nanocomposite. The particle size can be obtained from XRD and also from the recorded TEM images by calculating the average particle diameter through a statistical analysis counting about 200 particles considered to be spherical. UV/Vis Spectrophotometer is used to define the electronic structure and optical properties of the nanocomposite. The X ray Photoelectron Spectroscopy is used to study the composition of the nanocomposite through the determination of binding energy from all elements contained in the nanocomposite.

Application of TiO_2/QDs Nanocomposite

The TiO_2/QDs nanocomposite is a visible light active material, so it can be applied in many solar applications like photocatalyst, water splitting, and as semiconductor in solar cells device. The TiO_2/QDs nancomposite are widely used as many photocatalytic degradation reaction for cleaning water and air purifier. In degradation reaction of molecules, the holes generation by the proton (as shown in Figure 1) can react with the surface adsorbed H_2O to produce ·OH radicals that acts as hole scavengers to assist the electron-hole separation and preventing recombination. The holes can also directly oxidize the molecules into their radicals. In aerated system, the conduction band electrons are usually scavenged by O_2 to produce superoxide radical anions so both O_2 and the molecules are activated. The subsequent radical reactions that usually have low or no barriers will result the oxidative degradation molecules. TiO_2 is a most successful photocatalyst itself for heterogeneous photocatalytical organic waste degradation, but again its only UV light active limited its role so the use of TiO_2/QDs nanocomposite will surely enhance the photoactivity of pure TiO_2 as a catalyst for organic photodegradation reaction (Zhao *et al.*, 2008). Volatile waste degradation by TiO_2/QDs nanocomposite started from the surface modification by using more tolerant colour species, such as organic dyes, perovskite and QDs, can be used to construct stable photocatalyst material, which are able to degrade even colourless pollutant under visible light irradiation.

Over last decade, TiO_2 has been successfully developed to construct an overall water splitting system for continuously generation of hydrogen and oxygen in the absence of sacrificial reagents (Zou *et al.*, 2001). Currently, the available efficiency of water splitting technology production based on TiO_2 under visible light is still quite low due to its natural limited response to visible light, also because of fast charge recombination and backward reaction. Therefore, it needs to add electron donors to make up half of the water splitting reaction to reduce the backward reaction of H_2O to H_2. This electron donor will irreversibly consume photogenerated holes, thus preventing undesirable charge recombination (Antoniadou and Lianos, 2010).

The most sophisticated solar application of TiO_2/QDs nanocomposite is being applied in solar cells system to constract QDs-sensitized Solar Cells (QDSSC). The principle work of QDSSC is shown in Figure 4. QDSSC are based on ensembles of nanometer size interfaces between two semiconducting nanostructure materials where QDs are adsorbed to a wide band gap (commonly used TiO_2) through a linker with bifunctional molecules. Finally, a thin layer of liquid electrolyte containing redox couple or a hole conductor is sandwiched between two electrodes. The device configuration depicted in Figure 4 separates the positive and negative photogenerated carriers into different regions of the solar cell using the following mechanism: after incident photons are absorbed by the QDs, photoexcited electron-hole pairs are confined within the nanocrystal. If they are not separated quickly, they will simply recombine.

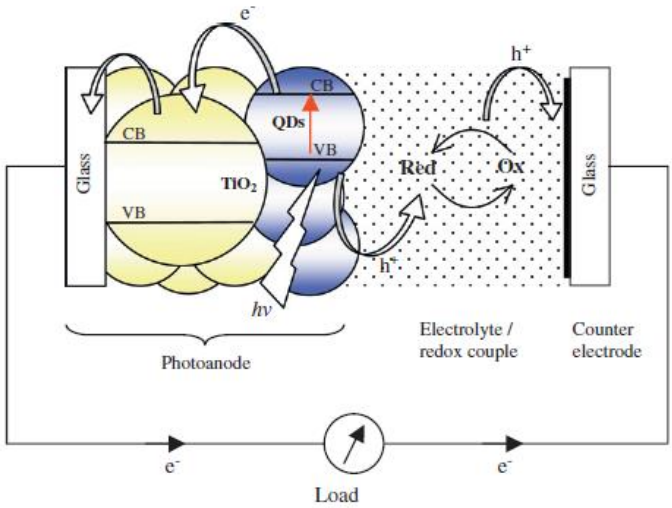

Figure 4 Work Principle of QDSSC (Jun *et al.*, 2013)

QDSSC is the most potential third generation photovoltaic technology to commercialize in wider application. However its overall efficiency so far are still very low comparing to other solar cells type. It still needs many improvement and development regarding to its efficiency and stability. Some efforts might be done to modify the architecture of QDSSC assembly for a better efficiency. It is including all QDSSC components such as QD material used and their sizes, choices of electron conductor for photoanode, counter electrode materials, electrolyte, and the surface engineering of the materials.

Conclusion

TiO_2/Quantum Dots nanocomposite materials have a great potent to solve the global energy, environmental, and economical problems. As improvement of dye-sensitized solar cells, quantum dots-sensitized solar cells is predicted to be the next generation technology to be developed as alternative energy supply. Quantum dots-sensitized TiO_2 is also potential for solar hydrogen production via water splitting, and as photocatalyst in dangerous pollutant degradation.

In order to enhance the solar device efficiency based on quantum dots sensitization and achieve commercialization, it needs further research on tailoring the nanostructures, to control the charge separation and transportation, to produce inexpensive catalyst and to study the reaction kinetics for the large scale commercialization.

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